THE DEVELOPMENT OF A CATHODIC CHARGING SYSTEM TO FORM HYDRIDES IN ZIRCALOY-4

An Undergraduate Research Scholars Thesis

by

RYAN ANTHONY BRITO

Submitted to Honors and Undergraduate Research
Texas A & M University
in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

Approved by
Research Advisor: Dr. Sean McDeavitt

May 2013

Major: Nuclear Engineering

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ABSTRACT

The Development of a Cathodic Charging System to Form Hydrides in Zircaloy-4. (May 2013)

Ryan Anthony Brito
Department of Nuclear Engineering
Texas A & M University

Research Advisor: Dr. Sean McDeavitt
Department of Nuclear Engineering

This project investigates several methods of electrochemical insertion of hydrogen into Zircaloy nuclear fuel cladding. These systems are being assembled at Texas A & M to form zirconium hydride in cladding to model crack propagation during storage in dry cask, determining the protective lifetime of the cladding. Hydride concentration profiles found in cladding before entering dry cask storage could not be duplicated using the system originally built in this project. Several modifications were made, including the introduction of a nitrogen bubbler, application of lead cathodes, and the refinement of set-up, and an additional hydrobisulfate ion bath system was built. Future work will further utilize these systems to attempt to replicate hydride profiles in spent fuel and apply samples in the development of a model to predict crack propagation through fuel cladding.

NOMENCLATURE

DHC	Delayed Hydride Cracking
DOE	Department of Energy
IAEA	International Atomic Energy Agency
wppm	Weight Parts Per Million

CHAPTER I

INTRODUCTION

In the United States nuclear industry, zirconium alloys serve three crucial purposes as fuel cladding: transferring heat, supporting the core during fission, and most importantly acting as a barrier between the fuel and coolant. During power production, waterside corrosion causes degradation of the cladding's mechanical properties through oxidation and hydrogen pick-up. Traditionally, burnt fuel bundles retired to a spent fuel pool awaiting permanent storage under the care of the United States' government. However, with the termination of funding for the Yucca Mountain Waste Repository, dry cask storage has had to address the need for extended on-site storage.[1]

Dry casks are sealed containers made of metal and concrete that contain used fuel after at least five years of cooling in the spent fuel pool, as shown in Figure 1.[1] As dry cask storage is meant as a temporary measure, on the order of several decades rather than the millennia required for transuranic fission products to decay sufficiently, the integrity of the fuel and cladding while in storage is of interest to ensure the fuel can eventually be removed from dry cask for transport to a permanent repository or reprocessing center.

The Department of Energy (DOE) has invested resources to determine the effects of the environment within dry cask storage on the integrity of the fuel assemblies over time. The objective of this project is to develop a method to insert hydrogen into Zircaloy-4 at hydride concentration profiles similar to high burnup fuel in dry cask storage for further study.

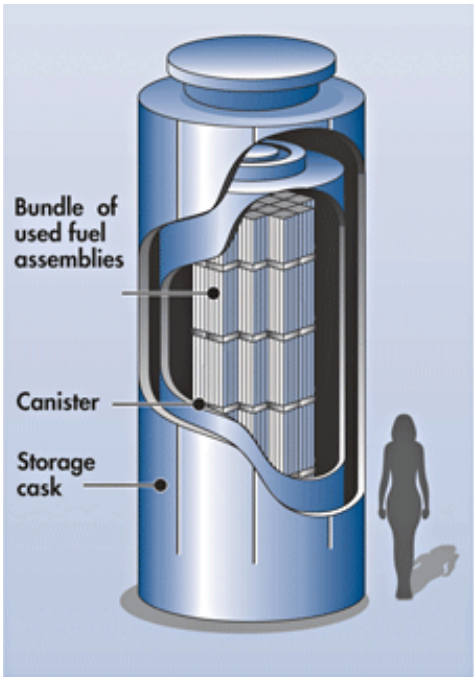

Figure 1. General Design of a Dry Cask Storage Unit[1]

Literature review

During oxidation of the fuel cladding during reactor operation, hydrogen is liberated and capable of diffusing into the alloy matrix.[2] If concentrations rise above the solubility level at a given temperature, as shown in Figure 2[3], zirconium hydride forms, causing embrittlement and increased risk of fuel cladding failure. Because the solubility limit decreases as temperature decreases, hydride formation is a particular problem during heat cycles, such as shutdown or drying of spent fuel, when soluble hydrogen precipitates up stress and thermal gradients. High stress zones can then induce delayed hydride cracking (DHC), or crack propagation along brittle hydride formations, causing cladding failure.[2]

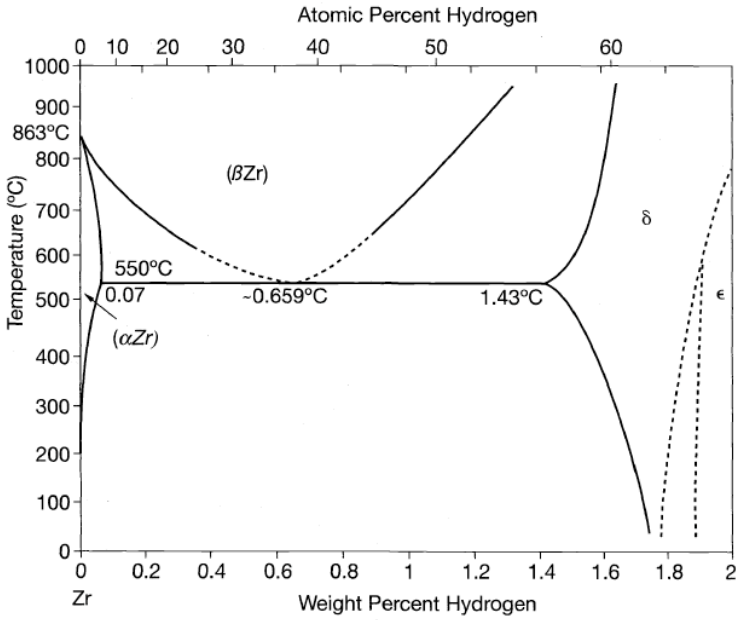

Figure 2. Phase Diagram for Zr-H[3]

At high burnup, hydrogen concentrations can be several hundred weight parts per million (wppm), forming dense hydride rims near the outer surface of the cladding and diffuse platelets throughout, as shown in Figure 3.[4] The hydride platelets in spent fuel are typically oriented circumferentially, making the cladding more brittle but not acting as crack propagators. However, before entering dry cask storage, the spent fuel goes through a drying process to prevent container corrosion, pressure changes, and increase fuel retrievability.[5]

The drying process typically involves heating spent fuel bundles in a low-pressure environment until stable vacuum, verifying water removal. The system is then backfilled with helium to allow additional water evolution. Heating for drying is provided by decay heat, and temperatures can reach over 250^{o}C, with a 400-570^{o}C regulatory limit.[5] These temperatures are significant enough to pull hydrogen back into solution within the cladding and change the hydrogen profiles significantly, as shown in Figure 4 and Figure 5.

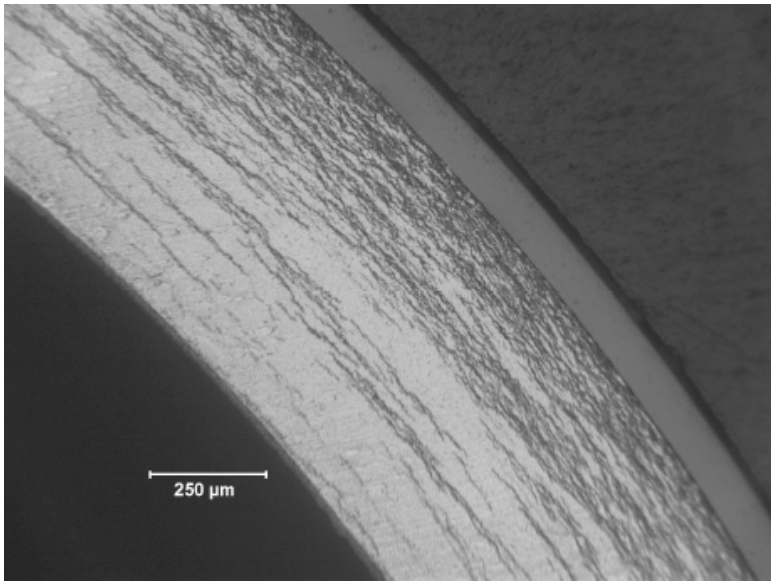

Figure 3. Zirconium hydride and oxide formations in irradiated Zircaloy-4 cladding (740 wppm)[4]

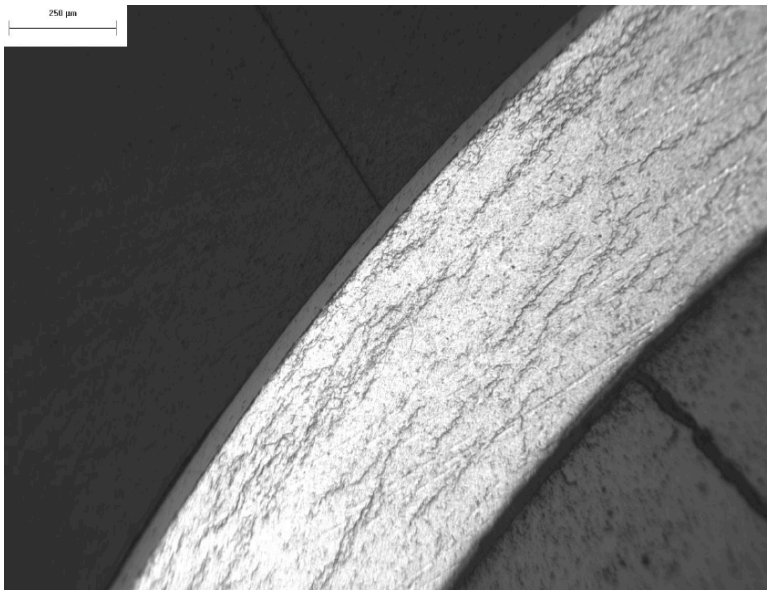

Figure 4. Zirconium hydride and oxide formations in irradiated, unstressed Zircaloy-4 cladding after drying (300 wppm)[6]

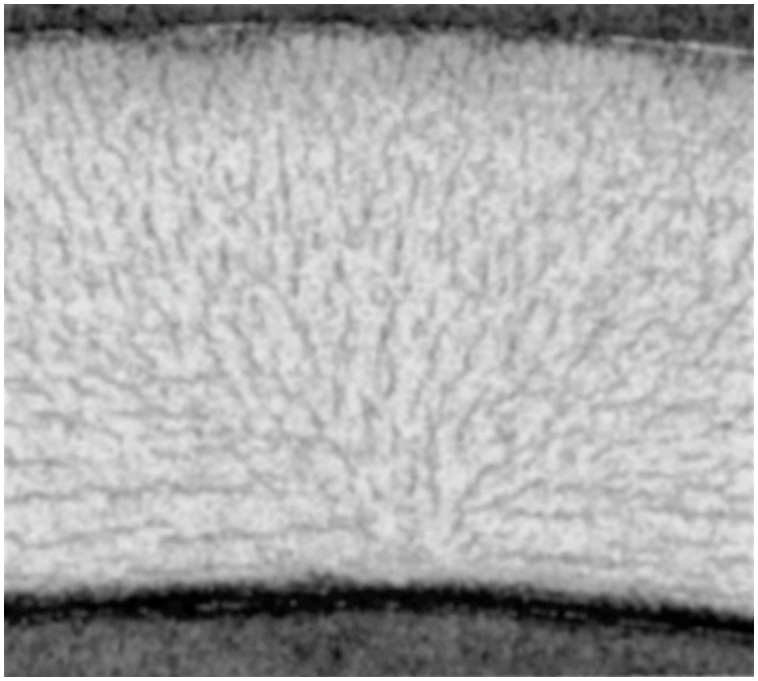

Figure 5. Zirconium hydride formations in Zircaloy-4 cladding after drying at 400^{o}C and 120 MPa radial stress (250 wppm)[7]

As shown in Figure 4, the heat treatment involved in drying can uniformly diffuse hydride formations throughout the cladding thickness at low enough concentrations. At higher concentrations, such as those at high burnup, the profile would be similar to Figure 3 with a dense ring of hydrides because the hydrogen is not completely soluble at the drying temperatures.[6] However, spent fuel drying and storage can also cause hydride reorientation, shown in Figure 5. During drying, internal pressure from fission gas can reorient hydrides radially. Radial hydrides increase the risk of cladding failure, acting as crack propagators.[7]

To study hydride reorientation as it relates to fuel retrieval from dry cask, several hydrogen insertion methods are available: actual spent fuel, static autoclave, gaseous diffusion, and electrochemical insertion. Spent fuel, while the most accurate at representing the hydrogen

profiles observed in dry cask, is subject to regulation and is difficult to handle and analyze. Static autoclave produces physically similar samples, relying on corrosion to provide hydrogen content, but takes significantly longer than other methods to provide similar hydrogen concentrations. Gaseous diffusion uses flowing hydrogen gas at elevated temperatures to produce a hydrogen concentration gradient and force diffusion into cladding. This method is complex compared to other methods and is dependent on the exclusion of oxygen, which buffers hydrogen ingress, from the system; however, gaseous diffusion is the most widely used method and achieves high hydrogen concentrations in short times. Finally, electrochemical insertion, the method explored in this project, uses electrolysis in the presence of ion baths or molten salts to force a hydrogen gradient near the surface of the cladding, causing diffusion. Electrochemical methods are characterized by their simplicity, are commonly used, and inexpensive. This project will study the application of several electrochemical methods for development at Texas A & M University.

A widely used electrochemical hydrogen deposition system distributed by the International Atomic Energy Agency (IAEA) is shown in Figure 6.[8] The system used a sulfuric acid electrolyte to produce hydrogen through electrolysis on the zirconium alloy cathode. The hydrogen diffused to form a dense hydride rim on the sample, which was annealed to disperse the hydrogen uniformly throughout the sample. According to Lepage et al., the system is capable of creating a hydride rim of 15 μm in 24 hours of varying hydrogen concentrations. The report continues to study the significance of DHC in Zr-2.5 Nb cladding, similar to this project for Zircaloy-4.

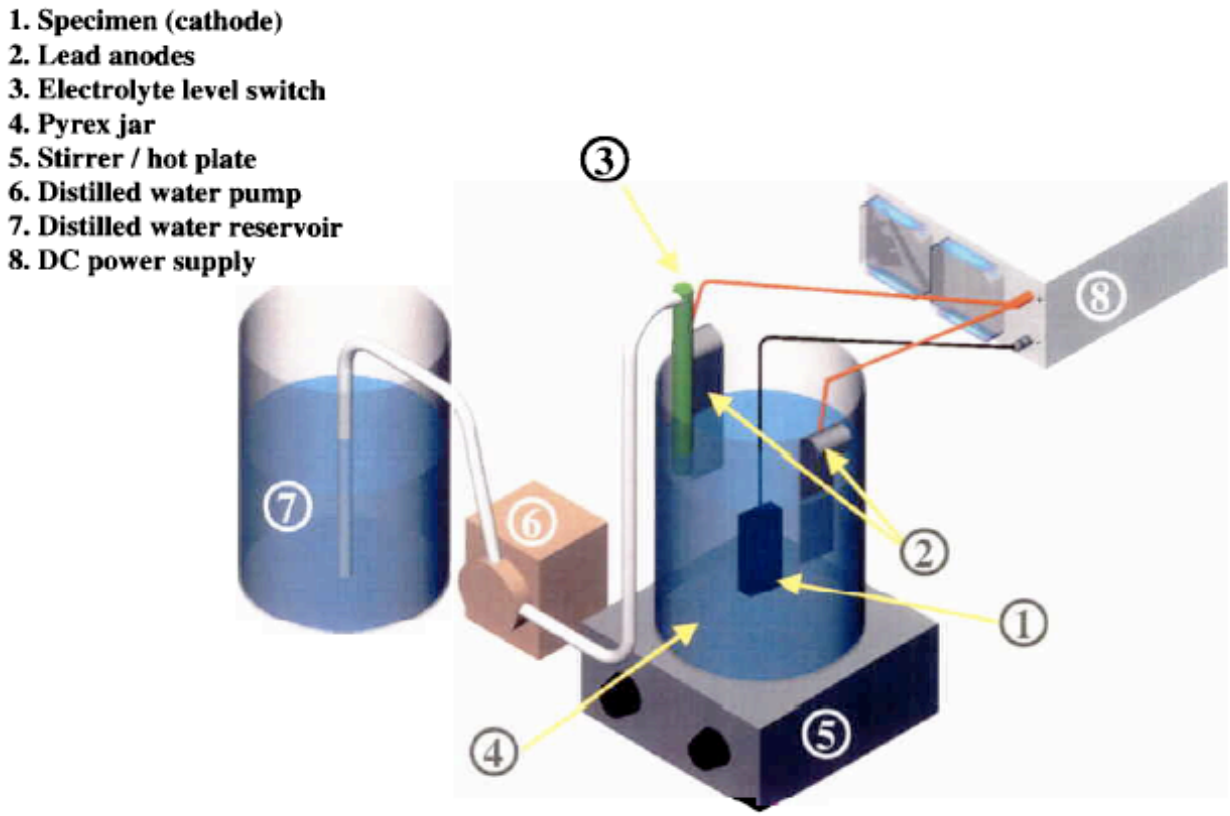

Figure 6. Electrochemical hydrogen deposition system developed by the IAEA to hydride zirconium alloy samples[8]

Another available electrochemical hydrogen deposition system is shown in Figure 7.[9] The system used an electrolyte containing several hydrobisulfate salts at 150°C to produce hydrogen through electrolysis on the zirconium alloy cathode. The hydrogen diffused to form a dense hydride rim on the sample, which was annealed to disperse the hydrogen uniformly throughout the sample in platelets. According to Choi et al., the system is capable of creating more than 1000 wppm of hydrogen in 24 hours.

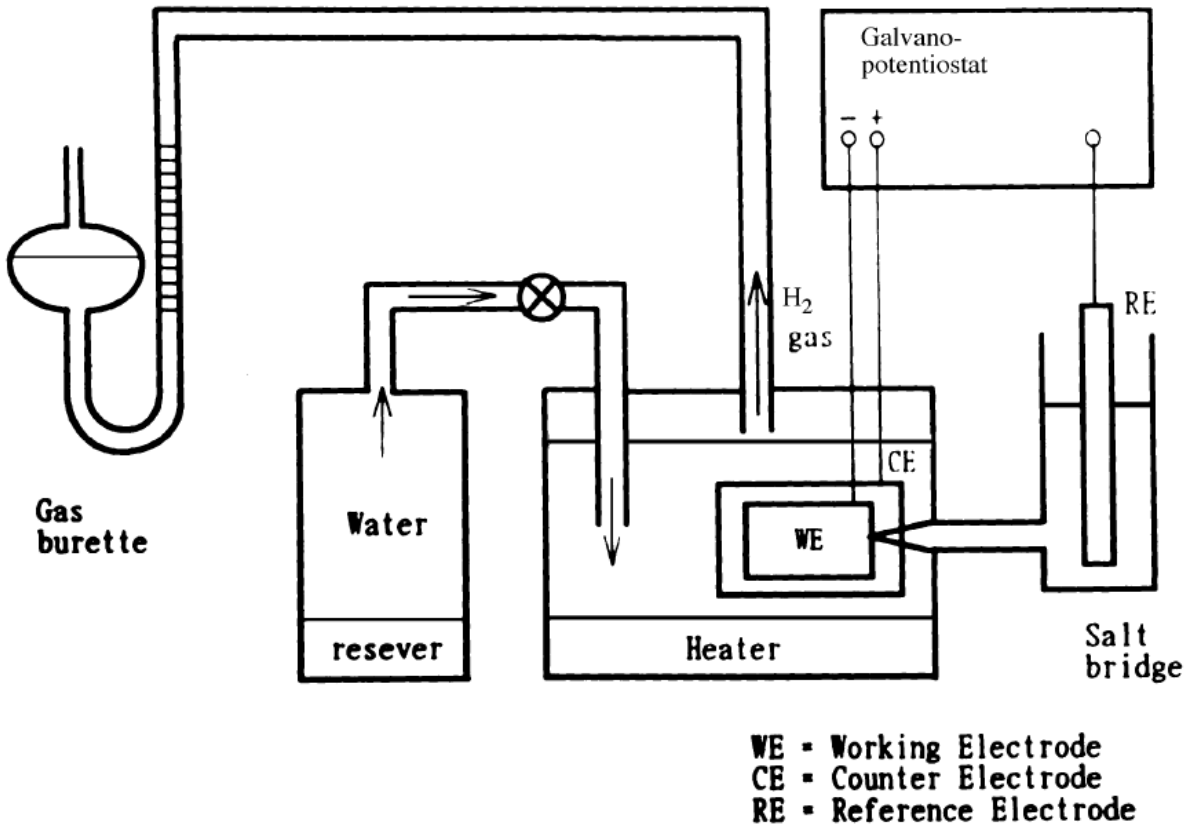

Figure 7. Electrochemical hydrogen deposition method using hydrobisulfate salts to hydride zirconium alloy samples.[9]

The final hydrogen deposition system being studied in this project is the molten salt system shown in Figure 8 developed by John, De, and Gadiyar.[10] The system utilized a molten salt mixture at 260°C shown in Appendix A with steam bubbled through the salt to electrolyze and create hydrogen. At low concentrations, the hydrides formed fine, randomly oriented precipitates, and at high concentrations, due to the high temperature utilized, the hydrides formed a dense layer at the surface and fine, randomly oriented precipitates at a concentration gradient. Following a heat treatment, the hydrides homogenized into platelets. The system was capable of producing 689 wppm of hydrogen in 6 hours.[10]

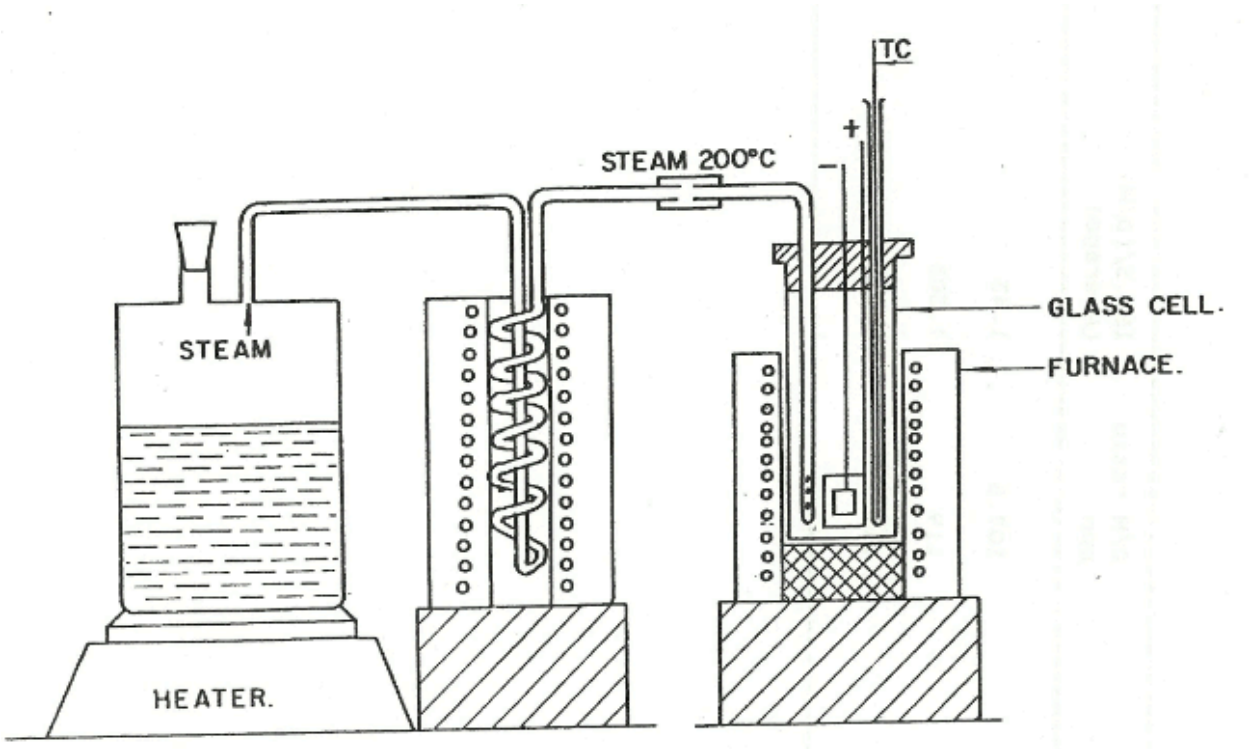

Figure 8. Electrochemical hydrogen deposition method using molten salts to hydride zirconium alloy samples.[10]

Objectives and motivation

The objective of this project is to investigate methods to insert hydrogen into Zircaloy-4 at hydride concentration profiles similar to high burnup fuel in dry cask storage and begin the assembly of these methods. As dry cask is a temporary storage measure, the integrity of the fuel needs to be preserved for future extraction. This project seeks to provide the support for further study into DHC, oxidation, and creep effects on fuel cladding integrity. Samples will be used to experimentally obtain data to help model crack propagation through fuel cladding. The model will be used to predict the protective lifetime of the cladding. The objective will be achieved by using an electrochemical method explored in the project and a tailored heat treatment to produce the profiles matching those seen in Zircaloy-4 after spent fuel drying.

CHAPTER II

METHODOLOGY

Due to the necessity for results and shortcomings of previous work, two methods of electrochemical hydrogen deposition will be used in this project: the Lepage and the Choi systems. The two systems will be developed in parallel and each seeks to produce the required hydrogen concentration profiles to mimic those in used fuel cladding. If results cannot be obtained with the Choi system, the molten salt system can be run within the same set-up. Following charging, the same procedures will be used to prepare the sample for microscopy. For this project, a non-standard zirconium alloy cladding will be used to assess the systems, and Zircaloy-4 will be used for final analysis to preserve quality assured material.

Lead anode sulfuric acid charging

The lead anode sulfuric acid charging set-up will be modeled after the Lepage design shown in Figure 6. Differing from the IAEA procedure, samples will initially be pickled for 5 minutes in an acid solution containing hydrogen peroxide, nitric acid, and hydrofluoric acid as shown in Appendix A. The purpose of the pickling procedure is to remove surface oxidation from ambient storage on the surface of the cladding, which is thought to inhibit hydrogen ingress. Before removal, the system will be set-up using a sulfuric acid electrolyte, the composition of which is listed in Appendix A, and pre-heated to 65^{o}C. Following removal and cleaning from the pickling solution, the sample will immediately be immersed into the electrolyte solution to reduce oxidation and the experiment started between 0.1 and 0.2 A/cm^2 of exposed surface area. Additional procedures and set-up requirements can be found in the IAEA document.[8]

Platinum anode hydrobisulfate salt charging

The platinum anode hydrobisulfate salt charging system will be modeled after the Choi design shown in Figure 7. Unlike the procedure followed by Choi, this project will use the pickling solution used above and shown in Appendix A for consistency and convenience. Similar to the previous approach, the system will be set-up prior to removal from the pickling solution to reduce surface oxidation. The parameters for the experiment are a 0.4 A/cm^2 current density at 150^oC in the hydrobisulfate ion bath shown in Appendix A. Additional procedure and set-up information can be found in the resource.[9]

Platinum anode molten salt charging

The platinum anode molten salt charging system will be modeled after the John design shown in Figure 8. Similar to the other systems, the pickling solution in Appendix A will be used. The parameters for the experiment are a 0.2 A/cm^2 current density near 260^oC in the molten salt solution shown in Appendix A with a 200^oC steam injection system. The molten salt system will be run at less than 260^oC due to a restriction for the integrity of the bubbler's tubing. Additional procedure and set-up information can be found in the resource.[10] For all methods, the relationship between charge duration and hydrogen content will be determined to better predict the outcomes of the experiments. The hydrogen content, profile, and geometry will be compared between the systems to compare the effects of the temperatures and approaches.

Microscopy preparation and analysis

Following charging, the sample will be sectioned in halves to compare the pre- and post-anneal hydride structures. Samples will undergo an annealing process at 400^oC for varying durations.

The annealing process serves to redistribute the dense hydride rim throughout the sample more similarly to used nuclear fuel cladding. To more closely approximate the concentration profiles, hydrogen content, increased hydrogen penetration, annealing duration, and rate of cooling following the annealing process will need optimization. For the study of crack propagation in a DHC model, annealing while the sample is under stress will also be studied. Annealing time, temperature, and force will be compared to the degree of reorientation in the sample.

After annealing, the samples will be cut using a diamond saw into a thin cylindrical cross-section. The cross-section, selected from the centerline of the sample to avoid edge effects, will be cold-mounted in epoxy and allowed to cure over night. Samples will then be polished to 1 μm and observed by optical microscopy to determine the quality of the polish. Using the hydride acid etch listed in Appendix A, the sample will be acid etched to reveal the hydride dispersion in the sample. The sample will then be analyzed at a microprobe visually and using x-ray diffraction mapping.

Microprobe images will be analyzed using ImageJ to determine hydride concentration throughout the cladding radius. To further characterize the hydrogen content, samples observed to have hydride formations will have additional cross-sections sent to outside vendors to measure the exact hydrogen content using the destructive technique of vacuum hot extraction. The hydrogen content will then be analyzed in comparison to the duration of charging and the final concentration profile.

CHAPTER III

RESULTS AND ANALYSIS

Ten charging sessions using the IAEA system with a platinum electrode, to reduce electrolyte-anode interaction, were completed. Following charging, samples were prepared along with a control sample of the original, uncharged stock material, a sample from previous work using a gaseous system, and a sample from another previous work using carbon cathodes. The results are shown in the micrographs labeled Figure 9 through 12.

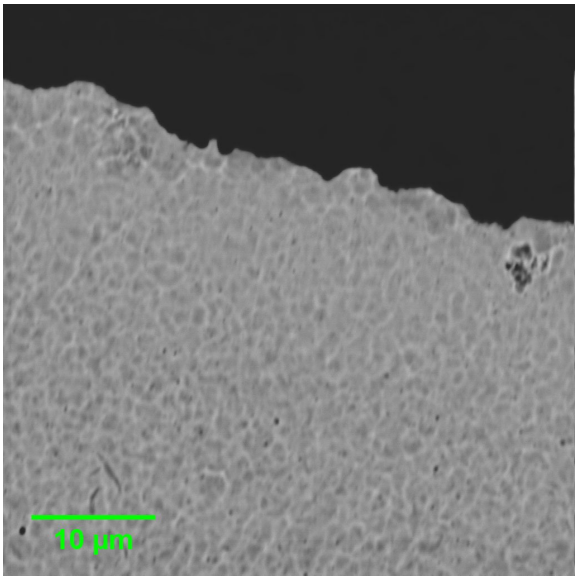

Figure 9. Backscattered electron image of a control sample used for validation in this project

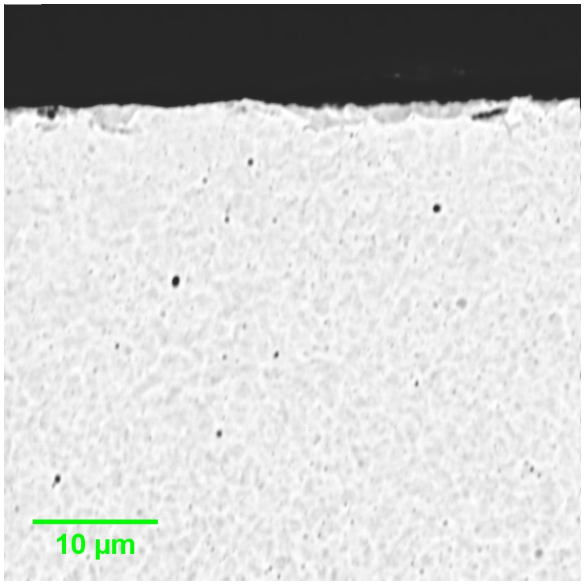

Figure 10. Backscattered electron image of sample charged in the IAEA system using a platinum electrode

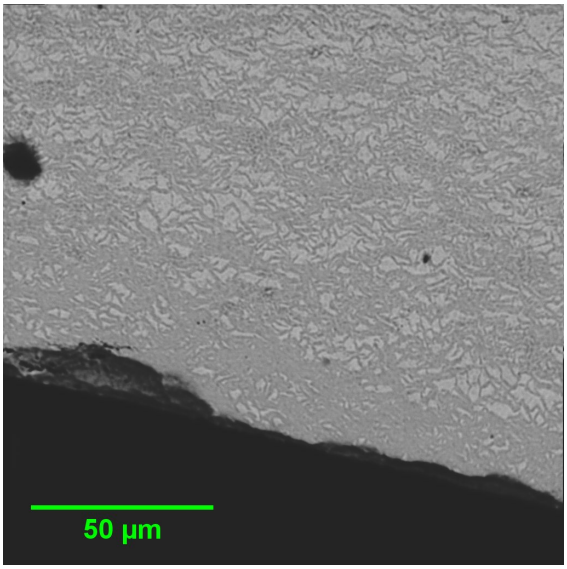

Figure 11. Backscattered electron image of previous work using a gaseous system showing diffuse hydride platelets

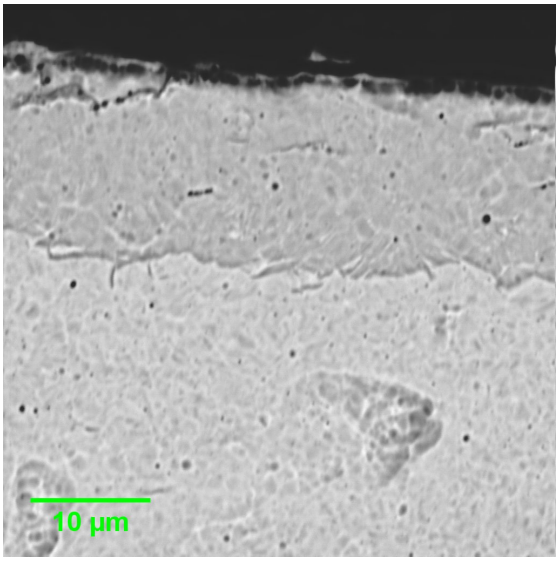

Figure 12. Backscattered electron image of previous work using carbon anodes showing a dense hydride rim

Compared to Figure 9, Figure 10, which is representative of all ten runs done in the IAEA system using the platinum electrode, shows no appreciable hydride formations. However, Figure 11 and Figure 12 display both diffuse and rim structured hydrides using the same sample preparation and microscopy techniques. While the charging system failed to force hydrogen pick-up in the Zircaloy cladding, the samples from previous work showed that the sample preparation technique is adequate to reveal hydride formations under microprobe microscopy.

In response to the inability to charge samples with hydrogen, three modifications were made to the system being run in order to potentially solve the mismatch between the literature and the system being used: the modifications were the introduction of a nitrogen bubbler, a lead anode, and a new method of attachment between the sample and the cathode wire. Samples are pickled before charging begins to eliminate the oxide layer, which acts as a barrier to hydrogen ingress. Addressing concerns that oxygen in solution within the electrolyte is capable of reforming the

oxide layer on the sample, the nitrogen bubbler was added to act as a getter for the oxygen. To better mimic the system used in the IAEA document, the lead electrode replaced the more inert platinum electrode previously used. Finally, the zirconium-niobium cathode wire was previously attached by wrapping the wire tightly around the outer circumference of the sample. Drilling a hole in the side of the sample and stringing the cathode wire through the hole replaced this method. Future work will focus on testing this system to determine if it can better force hydrogen pick-up in Zircaloy-4 samples.

In addition to the modifications made to the IAEA system, the development of the system used by Choi began. The assembly of the system is shown in Figure 13. To maintain compatibility with the molten salt system demonstrated by John, a steam bubbler is attached to help maintain the water level during operation. Calibrations relating the applied voltage to the furnace's output temperature were performed and are shown in Figure 14. Future work for this system will involve determining the parameters to ensure successful operation, including calculating the furnace setting to achieve a 150^{o}C ion bath temperature and the corresponding thermocouple reading, as well as attempting to charge samples with hydrogen and form the hydrogen profiles necessary to continue work on the project.

Figure 13. The bihydrosulfate ion bath charging system assembled at Texas A & M University

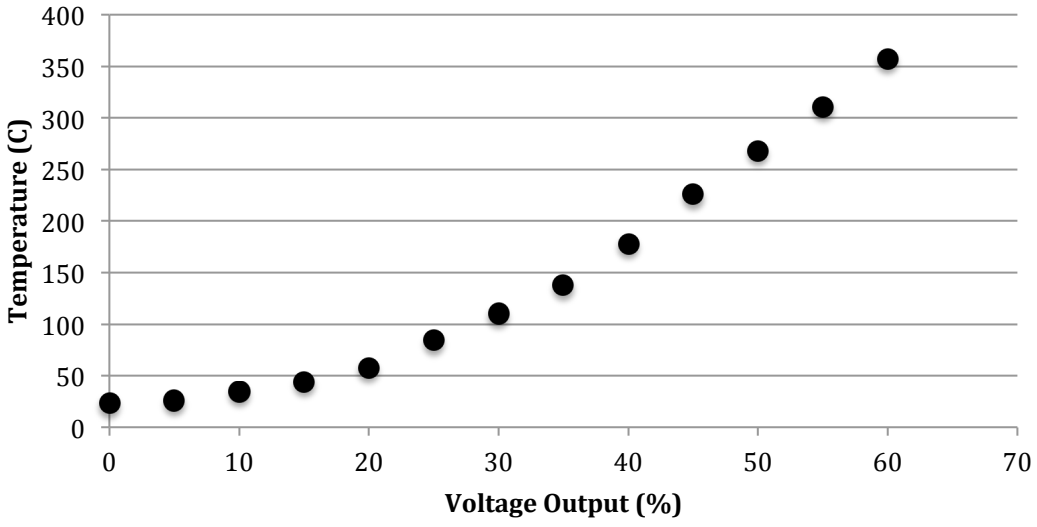

Figure 15. The relationship between the percent of voltage applied to the furnace and the output temperature

After proving a system can form hydrides within Zircaloy samples, future work will look to attach an in situ hydrogen content measurement system to charge samples to similar wppm hydrogen between experiments. For the development of the crack propagation model, research will also be done into crack starters during and before dry cask storage, the development of cracks through cladding, and methods and causes of movement of cracks. The frequency and rate of these mechanisms compared to the temperature, pressure, and time in dry cask storage can be used to develop a model relating hydrogen content and the dry cask environment to crack propagation through cladding, and thus the useful lifetime of dry cask storage as a temporary measure of spent fuel storage.

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APPENDIX A

Table I. Chemical inventory listing all the chemicals used in set-up and sample preparation along with the respective concentrations.

Chemical Name (Symbol)	**Concentration**
Hydrofluoric Acid (HF)	48%
Hydrogen peroxide (H_2O_2)	30%
Nitric Acid (HNO_3)	70%
Sulfuric Acid (H_2SO_4)	95-98%
Sodium Bisulfate ($NaHSO_4$)	Solid
Sodium Sulfate (Na_2SO_4)	Solid
Potassium Sulfate (K_2SO_4)	Solid

Table II. Various components and ratios of chemical inventory used in this project

	HF (mL)	**H_2O_2 (mL)**	**HNO_3 (mL)**	**H_2SO_4 (mL)**	**$NaHSO_4$ (mg)**	**Na_2SO_4 (mg)**	**K_2SO_4 (mg)**	**Distilled Water (mL)**	**$KHSO_4$ (mg)**
Pickling Solution	5	---	45	---	---	---	---	50	---
Sulfuric Bath	---	---	---	1	---	---	---	100	---
Salt Bath	---	---	---	---	500	50	10	100	---
Acid Etchant	2 drops	5	5	---	---	---	---	---	---
Molten Salt	---	---	---	---	250	37	75	---	250